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### A TECHNIQUE FOR MEASURING THE SOLUBILITIES OF GASES IN LIQUIDS

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## **TECHNICAL REVIEW AND APPROVAL**

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The experiments reported herein were conducted according to the principles set forth in the current edition of the "Guide for the Care and Use of Laboratory Animals," Institute of Laboratory Animal Resources, National Research Council.

This technical report has been reviewed by the NMRI scientific and public affairs staff and is approved for publication. It is releasable to the National Technical Information Service where it will be available to the general public, including foreign nations.

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## INTRODUCTION

Decompression sickness (DCS) in divers is presumed to result somehow from the accumulation of dissolved inert gases in tissue, which must occur during periods of increased ambient pressure, i.e. during dives. It seems likely that bubbles produced during or after decompression constitute at least one of the direct causes of DCS symptoms. The risk of decompression sickness, therefore, may depend in part on the solubilities of inhaled gases in biological fluids and tissues. Quantitative prediction of DCS risk may be aided by the availability of measured values of these solubilities over a range of partial pressures relevant to divers.

The techniques employed for measuring liquid/gas equilibria usually involve removing an aliquot of one of the phases after equilibration. The composition of this aliquot is assayed and the composition of the other phase is then computed by mass balance. The necessary equilibration time is determined empirically. Most of the various experimental methods have differed fundamentally only in the type of assay chosen: gas chromatography (1-8), mass spectrometry (9-11), radioassay (12,13), and dilatometry (14,15). The dilatometric assay consists of reducing the pressure on a liquid aliquot and then holding it at that reduced pressure; this is done by expanding the vessel containing the aliquot as gas desorbs from the liquid phase. The expansion can be accomplished by adjusting the piston in a syringe barrel that constitutes part of the volume of the gas phase above the liquid aliquot. One computes the amount of desorbed gas from the necessary volume increase and then computes the composition of the two phases by mass balance. This method therefore requires two equilibrations rather than one, which provides additional sources of uncertainty in the calculation of solubility.

A simpler technique for measuring liquid/gas equilibria dispenses with the need for separating an aliquot of material and thereby has the potential for greater precision. In this method a liquid sample in a closed vessel is compressed to a known pressure, either by forcing gas into the vessel or by decreasing the vessel's volume. After equilibration, the pressure in the 5

vessel is measured again. The amount of gas adsorbed by the liquid can be calculated from the pressure change that occurs during equilibration (16,17).

The published reports of gas solubility that we have reviewed are universally marred by the authors' failure to evaluate either the accuracy or the precision of their measurements using a formal error analysis. In particular, there is no evidence that the authors measured gas leakage from their systems or that they made a quantitative assessment of leakage as a source of biased error.

We are instituting an investigation designed to measure the solubilities of nitrogen, helium, and other diving gases in water, blood, and various solid tissues at 37°C and pressures between 1 and 10 atm. Solubilities will be measured using the last technique mentioned above: the pressure change that occurs in a closed system during interphase equilibration will be measured after an abrupt change in system pressure has been effected. The experimental plan is described in the next section; it is briefly summarized as follows. Two identical vessels immersed in a water bath at 37°C are bridged by a high-precision differential pressure transducer and also by a tube that bypasses the transducer. One vessel contains a measured amount of water or tissue along with gas, and the other contains only gas. Prior to an experiment, with the tube between the vessels opened, sufficient time is allowed for 1) the contents of both vessels to reach 37°C, 2) the gas phase of both vessels to reach the dew point through gradual evaporation of some of the water, and 3) the condensed phase to equilibrate with the gas phase at 37°C and known initial pressure (equal to the ambient pressure if the system is in communication with air; otherwise, equal to the gauge pressure plus ambient pressure). The initial conditions of the experiment are thereby established. At the start of the experiment the two vessels are simultaneously pressurized and the vessels then are closed off from each other. Sufficient time for reequilibration is allowed, and the pressure difference between the vessels is read from the differential transducer. The amount of gas dissolved in the liquid or tissue is calculated from this pressure differential.



In this report the experimental method and the means of analyzing the data are discussed. Since chemists, physicists, and engineers commonly consider gas/liquid equilibria in terms of Henry's Law or deviations from Henry's Law, we include a detailed derivation for the equation to calculate the Henry's Law coefficient from the results of the experiment. We also show how to compute the Ostwald coefficient, since it has broader application in biological systems than does the Henry's coefficient. Sources of error and means of limiting them are discussed quantitatively. This intensive error analysis is necessary in order to ensure the accuracy of the planned solubility measurements.

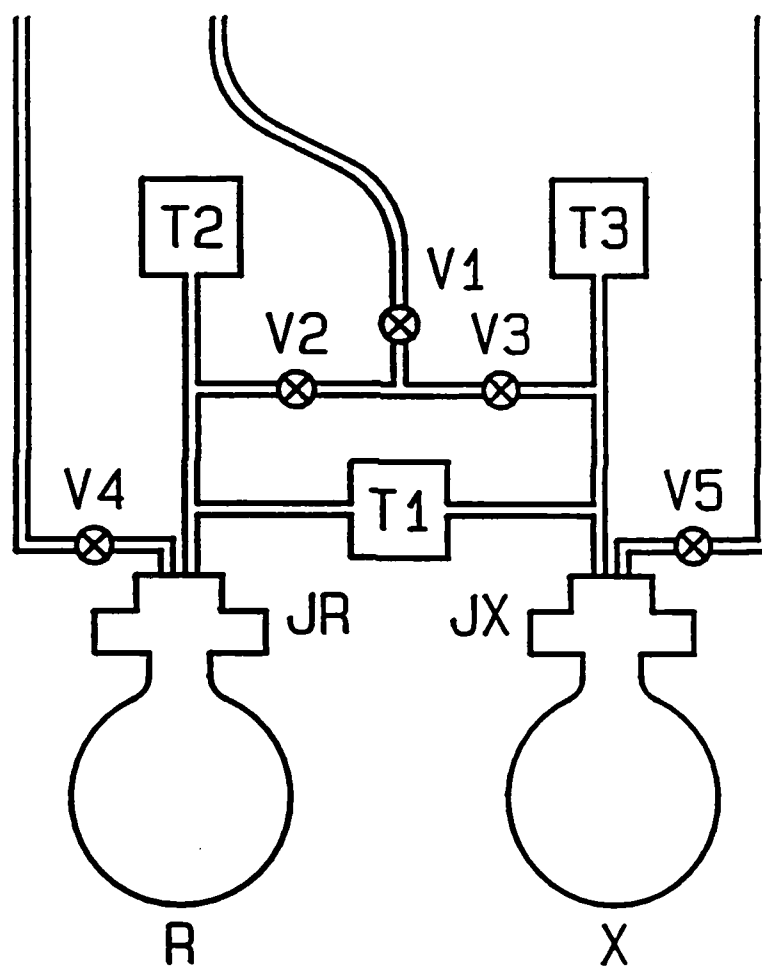
### Experimental method

The experimental apparatus is diagrammed in Fig. 1. Two vessels and a system of stainless steel tubing are immersed in an insulated water bath maintained at  $37 \pm 0.05^\circ\text{C}$  by exchange with a heated supply bath. The temperature of the water bath is monitored by a thermistor whose calibration is updated periodically using a mercury thermometer certified by the National Bureau of Standards. The immersed portion of the system is symmetrical about a differential pressure transducer (T1 in the diagram) and a valve (V1 in the diagram) through which gas can be fed from a cylinder. Valves V2 and V3 allow communication between the vessels and valve V1; valves V4 and V5 allow communication between the vessels and the atmosphere. Each vessel is always in communication with the differential transducer and each vessel is penetrated by a pressure transducer referenced to the atmosphere (T2 and T3).

All of the pressure transducers are calibrated using a dead-weight standard from CEC Instrument Company (Pasadena, California). Appendix A contains a listing of the components used in this experiment and their specifications. The procedure we will use for measuring gas solubility in a condensed phase is as follows.

A sample of known volume of the condensed phase is loaded into what we shall call the "experimental" or "X" vessel, whose volume has been measured by the procedure discussed in Appendix B. Flask "R" is a "reference" vessel containing no condensed phase. The condensed phase might consist of water, blood, or an isotonic saline solution containing bits of tissue. In some experiments the condensed phase will be allowed to equilibrate with air at  $37^\circ\text{C}$  and ambient pressure by leaving valves V2, V3, and V5 opened, and valves V1 and V4 closed. If the condensed phase must be equilibrated with some gas other than air, the system will be purged with the desired gas. Valve V5 then will be closed, and the condensed phase will be allowed to equilibrate with the gas phase. In either case, the system is left undisturbed overnight to allow the gas phase to become humidified at  $37^\circ\text{C}$ . This time is more than sufficient for the gas in both flasks and in the intervening tubing to closely

**FIGURE 1**  
**THE SOLUBILITY APPARATUS**



approach the dew point by passive diffusion of the water vapor evolved at the liquid surface. This statement is supported by drawing the analogy between mass transfer and heat transfer and using published solutions for the unsteady-state heating of a homogeneous bar. The solution for an infinitely long bar heated at one end is especially useful because it is certain to underestimate the humidification rate in our finite system, and therefore we can say confidently that it provides a conservative estimate of the necessary humidification time. For the details of these solutions the reader is referred to chapter 11 of Bird, Stewart, and Lightfoot (18).

A magnetic stirring bar is used to agitate the contents of the X vessel during the equilibration period, in order to minimize transport resistance in the condensed phase. After being left overnight the system has the following conditions: 1) the system is at 37°C, 2) the gas phase in both vessels is saturated with water vapor, and 3) the condensed phase is equilibrated with the gas phase at a known initial pressure (i.e., the barometric pressure plus the gauge pressure). These constitute the initial conditions for the experiment. The barometric pressure is measured using a mercury manometer referenced to vacuum. To begin the experiment, a pure, dry gas is injected quickly into the system by opening valve V1 (valve V5 is closed first if it had been open overnight). The injection must be completed within a few seconds to ensure negligible diffusion of gas into the condensed phase during initial pressurization. The symmetry of the system should ensure that the two vessels are pressurized equally. The tubing has a high enough length-to-diameter ratio to preclude appreciable backmixing, so that no material should leave the system during the pressurization. After pressurization, valves V2 and V3 are closed simultaneously to isolate the flasks from one another. The contents of the X vessel are stirred continuously during the experiment. The system is allowed sufficient time to reequilibrate and then the following information is recorded: (1) the indicated pressure difference between vessels R and X and (2) the gauge pressure in vessel R. The barometric pressure is measured again so that the

gauge pressure can be converted to absolute pressure. Next, valves V4 and V5 are opened simultaneously so that both vessels are vented to the atmosphere and the pressure across any one of the transducers becomes zero. The offset voltage of each transducer (i.e., the indicated voltage at zero differential pressure) is recorded and its value is used to adjust the transducer reading taken a moment earlier, thereby minimizing response drift as an error source.

The pressure difference between the X and R sides is a function of the amount of gas that dissolves during the experiment. The placement of the differential transducer between two pressurized flasks means that the pressure across it is much lower than the absolute pressure on either side. This allows us to use a differential transducer rated for a maximum differential pressure of only 1000 mmHg (1.3 atm) at absolute pressures of up to 10 atm. The injection of a pure, dry gas at the start of the experiment effects a change in the partial pressure of the injected gas only. Other gases, e.g. oxygen and water, do not undergo a change in partial pressure. In an ideal system, where by definition the solubilities depend only on the partial pressures of the solutes, oxygen, water, and any other miscellaneous gases will undergo zero net interphase transport during the experiment and will have no effect on the final differential pressure.

Part II of "Data analysis" will explain how the information obtained in the experiment described above can be used to calculate gas solubility.

## Data analysis

### I. Theory: Equilibria of sparingly soluble gases

Discussions in this section are adapted from Prausnitz (19).

The analysis of phase equilibria is greatly simplified by reducing the pressure-volume-temperature information to a single parameter, the fugacity, which has units of pressure. The fugacity is defined such that, at equilibrium, its value for each chemical species is the same in all phases.

Thus, for a two-phase, two-component system,

$$f_1^A = f_1^B \quad [1a]$$

$$f_2^A = f_2^B \quad [1b]$$

where superscripts A and B refer to the two phases and subscripts 1 and 2 refer to the two species. For solutions of gases in liquids equation [1] is usually rewritten in the following form for the solute, which we denote by the subscript "2":

$$f_2 = \phi_2 y_2 P = \gamma_2 x_2 f_2^0 \quad [2]$$

where  $\phi_2$  = fugacity coefficient for the solute in the gas phase

(dimensionless);

$y_2$  = mole fraction of the solute in the gas phase (dimensionless);

$P$  = total pressure (mmHg);

$\gamma_2$  = activity coefficient of the solute in the liquid phase

(dimensionless);

$x_2$  = mole fraction of the solute in the liquid phase (dimensionless);

$f_2^0$  = fugacity of the solute at some arbitrary reference state (mmHg).

The value of the activity coefficient  $\gamma_2$  depends on the value of  $f_2^0$  at the chosen reference state. For an ideal gas the fugacity coefficient is identically 1.0, and for a liquid solution that is ideal in the Henry's Law

sense  $\gamma_2$  is independent of  $x_2$ . Then, for an ideal system equation [2] becomes "Henry's Law":

$$y_2 \phi = H x_2 \quad [3a]$$

$$\text{with} \quad H = \gamma_2 f_2^0 \quad [3b]$$

where  $H$  is the Henry's Law coefficient (mmHg/mol fraction) and is independent of pressure. The Henry's coefficient is empirically determined. For any liquid/gas system there is a pressure below which Henry's Law is valid. On a molecular level, at low mole fractions a solute molecule "sees" only solvent molecules and therefore its environment does not change appreciably with changes in the mole fraction; this accounts for the constancy of the activity coefficient and the wide validity of Henry's Law for sparingly soluble gases.

At sufficiently high pressures we can expect non-ideal behavior in either phase (or both). In the gas phase the fugacity coefficient of a component in a mixture is given by the following exact relation, which is of general validity:

$$RT \ln (\phi_i) = \int_V^\infty \left[ \left( \partial \phi / \partial n_i \right)_{T,V,n_j} - (RT/V) \right] dV - RT \ln (z) \quad [4]$$

where  $R$  = gas law constant (mmHg·cm<sup>3</sup>)/(gmol·K);

$T$  = absolute temperature (°K);

$\phi$  = total absolute pressure (mmHg);

$V$  = volume of gas phase (cm<sup>3</sup>);

$n_i$  = number of moles of the species of interest in the gas phase (gmol);

$n_j$  = number of moles of any other species in the gas phase (gmol);

$z$  = compressibility factor =  $PV/nRT$  (dimensionless).

To evaluate the integral in equation [4] we need either (1) a state function for the solute (i.e., a P-V-T equation) that is explicit in pressure or (2) compressibility data at the temperature of interest that are sufficient to permit numerical integration. For evaluating the pressure dependence of the solute fugacity in the liquid phase, the Krichevsky-Kasarnovsky equation

is valid if  $x_2$  is sufficiently small and the solution is well below its critical temperature:

$$\ln(\gamma_2 f_2^0) = \ln(f_2/x_2) = \ln(H | P_2 - P_1^s) + [v_2^m (\phi - P_1^s)]/RT \quad [5]$$

where  $(H | P_2 - P_1^s)$  = Henry's coefficient evaluated at the vapor pressure of the solvent (mmHg/mole fraction);

$v_2^m$  = molar volume of the solute in the liquid phase at infinite dilution ( $\text{cm}^3/\text{gmol}$ );

$P_1^s$  = vapor pressure of the solvent at the solution temperature (mmHg).

Equation [5] has been shown to agree excellently with the data on nitrogen and hydrogen in water at pressures as high as 1000 atm. Combining equations [2], [4], and [5] we find that we can relate  $y_2^0$  to  $x_2$  using the following proportionality factor:

$$y_2^0/x_2 = H_{\text{eff}} = \frac{\exp \left[ \ln(H | P_2 - P_1^s) + [v_2^m (\phi - P_1^s)]/RT \right]}{\exp \left[ \left( 1/RT \right) \int_V^\infty \left[ \left( \partial \phi / \partial n_1 \right)_{T,V,n_2} - (RT/V) \right] dV - \ln z \right]}$$

where we define  $H_{\text{eff}}$  as an "effective" Henry's coefficient. For ideal systems the complicated expression on the right hand side becomes a constant equal to  $H$ , and the above relation decomposes to equation [3], Henry's Law. Therefore, a plot of  $y_2^0$  versus  $x_2$  is linear within the Henry's Law region and curved at higher pressures.



## II. Computation of the Henry's Law coefficient

The nomenclature for this section is listed in Appendix C.

Initial conditions on the X vessel (the one containing two phases):

Conservation of the inert gas at the start of the experiment leads to

$$n_{\text{total}}^0 = n_L^{0-} + n_G^{0+} \quad [6]$$

That is, just after the pressurization at time = 0, the liquid phase is still equilibrated with gas at the old pressure  $\phi^{0-}$  but the gas phase is at the new pressure  $\phi_X^{0+}$ . Assuming the mole fraction of the solute is small enough that  $(n_1+n_2)=n_1$ , we can rewrite equation [6] in terms of observable quantities as

$$\begin{aligned} n_{\text{total}}^0 = & [(V_L \rho_L)/(H^{0-} M_1)] (\phi^{0-} - P_1^{0-} - P_{\text{oth}}^{0-}) \\ & + [V_G/(z_X^{0+} RT^{0+})] (\phi_X^{0+} - P_1^{0+} - P_{\text{oth}}^{0+}) \end{aligned} \quad [7]$$

The Henry's coefficient H can be what we shall call an "effective Henry's coefficient" if Henry's Law is not actually valid at pressure  $\phi^{0-}$ . We define an effective Henry's coefficient as

$$H_{\text{eff}} = y_2 \phi/x_2 \quad [8]$$

without making the fundamental assumption of Henry's Law, which is that H is independent of pressure.

We can simplify equation [7] somewhat by recognizing that the system temperature should equal the water bath temperature both before pressurization and a long time after pressurization, so that

$$T^{\infty} = T^{0-} \quad [9]$$

Therefore, we can discard the superscripts on T that denote times 0- and  $\infty$ . Further, we assume that gases other than the test gas and the solvent

vapor are present at low enough partial pressures that they behave ideally. The following then holds true for their portion of the gas phase:

$$P_{oth}^{0+} = (T^{0+}/T^{0-}) P_{oth}^{0-} = (T^{0+}/T^*) P_{oth}^{0-} \quad [10a]$$

Also, provided the system pressurization is accomplished quickly enough that there is only negligible evaporation of solvent or condensation of solvent vapor between time = 0- and time = 0+, then we can write an analogous equation for the partial pressure of solvent vapor:

$$P_1^{0+} = (T^{0+}/T^{0-}) P_1^{0-} = (T^{0+}/T^*) P_1^{0-} \quad [10b]$$

Substituting equations [9] and [10] into equation [7] yields

$$\begin{aligned} n_{total}^{0+} = & [(V_L \rho_L)/(H^{0-} M_1)](\phi^{0-} - P_1^{0-} - P_{oth}^{0-}) \\ & + [V_G/(z_X^{0+} RT^{0+})] \phi_X^{0+} - [V_G/(z^{0+} RT^*)](P_1^{0-} + P_{oth}^{0-}) \end{aligned} \quad [11]$$

Final conditions on the X vessel: To describe the contents of vessel X after the two phases have been in contact for a long time we have the following expressions, which are analogous to equations [6] and [7]:

$$n_{total}^* = n_L^* + n_G^* \quad [12]$$

and

$$\begin{aligned} n_{total}^* = & [(V_L \rho_L)/(H^* M_1)](\phi_X^* - P_1^* - P_{oth}^*) \\ & + [V_G/(z_X^* RT^*)](\phi_X^* - P_1^* - P_{oth}^*) \end{aligned} \quad [13]$$

To allow for leakage from the "X" vessel we shall define parameter  $f_X$  as follows:

$$f_X = n_{total}^* / n_{total} \quad [14]$$

As defined,  $f_X = 1$  for a perfectly-sealed vessel and  $f_X < 1$  if there is a finite leak when the vessel's contents are compressed above ambient pressure. We can rearrange equation [14] to obtain the following mass balance around the "X" vessel, which incorporates the possibility of leakage:

$$n_{\text{total}}^{\infty} = f_X n_{\text{total}}^{0-} \quad [15]$$

To the extent that Henry's Law correctly describes the behavior of gases other than the test gas and the solvent vapor, and leakage is absent, their partial pressures are the same at time  $= \infty$  as it at time  $= 0-$ . This is because 1) there is no transport of these miscellaneous gases across system boundaries between those times and 2) the system temperature is the same at both times. If leakage does occur, Henry's Law indicates that the proportionality between  $P_{\text{oth}}$  and  $x_{\text{oth}}$  remains unchanged, from which it follows that

$$P_{\text{oth}}^{\infty} = f_X P_{\text{oth}}^{0-} \quad [16]$$

according to the definition of  $f_X$  given by equation [14]. We also assume that there is no change in the partial pressure of solvent vapor during the experiment, which is to say that the solvent evaporates as quickly as it leaks from the vessel, as would certainly be the case except when the leak is disastrously large or the solvent quite nonvolatile.

R vessel: We now consider the "R" or "reference" vessel, which contains only a gas phase. Since it is a rigid vessel, the following pressure-temperature relation is true for its contents:

$$\frac{P_R^{\infty}}{Z_R^{\infty} n_R^{\infty} T^{\infty}} = \frac{P_R^{0+}}{Z_R^{0+} n_R^{0+} T^{0+}} \quad [17]$$

We shall allow for leakage from vessel R as well as from the other, and we define a leak coefficient  $f_R$  as follows:

$$f_R = n_R^{\infty} / n_R^{0+} \quad [18]$$

Substitution of equation [18] into equation [17] and rearrangement of the result yields an expression for  $T^{0+}$ :

$$T^{0+} = \frac{\phi_R^{0+} z_R^{\infty} f_R T^{\infty}}{\phi_R^{\infty} z_R^{0+}} \quad [19]$$

Both vessels: Finally, the pressure difference between the two flasks is known at time infinity and can be used to eliminate  $\phi_X^{\infty}$  from the equations:

$$\Delta P^{\infty} = \phi_R^{\infty} - \phi_X^{\infty} \quad [20]$$

Further, at time  $0+$  both vessels have the same temperature  $T^{0+}$  and pressure  $\phi^{0+}$ , and therefore the same compression factor  $z^{0+}$ , and so the subscript denoting which vessel we are considering can be omitted. We now can obtain the desired expression for the Henry's coefficient  $H$  by combining equations [11], [13], [15], [16], [19], and [20], which is straightforward:

$$H^{\infty} = \frac{\alpha_1 (\phi_R^{\infty} - \Delta P^{\infty} - P_1^{\infty} - f_X P_{oth}^{0-})}{(f_X / H^{0-}) \alpha_1 (\phi^{0-} - P_1^{0-} - P_{oth}^{0-}) + \alpha_2 \alpha_3} \quad [21]$$

where  $\alpha_1 = \rho_L V_L / M_1$

$\alpha_2 = V_G / RT^{\infty}$

$\alpha_3 = (f_X / f_R) \phi_R^{\infty} / z_R^{\infty}$   
 $- (\phi_R^{\infty} - \Delta P^{\infty} - P_1^{\infty} - f_X P_{oth}^{0-}) / z_X^{\infty} - f_X (P_1^{0-} + P_{oth}^{0-}) / z^{0+}$

Thus, when the system is not ideal, meaning that the "effective" value of  $H$  depends on pressure,  $H_{eff}^{\infty}$  can be computed using equation [21] providing that we know the value of the Henry's coefficient at pressure  $\phi^{0-}$ .

If  $H$  is independent of pressure, that is, if the system is within the Henry's law region at both pressure  $\phi^{0-}$  and pressure  $\phi^{\infty}$  then we may substitute

the relation  $H^* = H^{0-}$  into equation [21] and rearrange to yield

$$H = \frac{\alpha_1 \alpha_4}{\alpha_2 \alpha_3} \quad [22]$$

where  $\alpha_4 = (\phi_R^* - \Delta P^* - P_1^*) - f_X (\phi^{0-} - P_1^{0-})$

and  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  are as defined for equation [21].

It is interesting to note that  $\phi^{0+}$  has disappeared from the equations altogether. The reason is that, since both sides of the apparatus are elevated quickly to the same pressure at time = 0, the initial differential pressure is zero. If the apparatus consisted of only one vessel, then knowledge of the total pressure at time = 0+ would be required for solving for H. As it is, the final differential pressure ( $\Delta P^*$ ) describing the change in pressure of the system due to absorption, the final total pressure ( $\phi_R^*$ ), and the initial total pressure at time 0- ( $\phi^{0-}$ ) are sufficient for defining the system.

### III. Computation of the Ostwald coefficient

Henry's law is commonly encountered in studies of the thermodynamics of gas/liquid systems. Therefore, equations for computation of Henry's coefficient were derived in the previous section. However, computation of the Henry's coefficient requires knowledge of the mole fraction of solute in the condensed phase, which is possible only if one knows the average molecular weight of the solvent, and one cannot expect to determine this for a tissue sample. For tissue samples we instead compute the Ostwald coefficient  $\Gamma$ , defined as follows:

$$\Gamma_{2,1} = (\text{volume of dissolved gas "2", evaluated at 1 ATA and the experimental temperature}) \text{ per } (\text{volume of condensed phase "1"}).$$

Note that  $\Gamma_{2,1}$  is never pressure-independent; in the Henry's Law region  $\Gamma_{2,1}$  is directly proportional to  $P_2$ .

From the above discussion we deduce the following expressions for the number of moles of dissolved gas at time 0- and time  $\infty$  in our experiment:

$$n_L^{0-} = \frac{(1 \text{ ATA}) V_L}{R T^\infty z_{1 \text{ ATA}}} \Gamma^{0-} \quad [23a]$$

$$n_L^\infty = \frac{(1 \text{ ATA}) V_L}{R T^\infty z_{1 \text{ ATA}}} \Gamma^\infty \quad [23b]$$

Given that Henry's Law is valid ( $\Gamma_{2,1}$  is directly proportional to  $P_2$ ) at the pressure  $\phi^{0-}$ , we can write the Ostwald coefficient at time 0- as

$$\begin{aligned} \Gamma^{0-} &= \Gamma_{1 \text{ ATA}} P_2^{0-} / (1 \text{ ATA}) \\ &= \Gamma_{1 \text{ ATA}} (\phi^{0-} - P_1^{0-} - P_{\text{oth}}^{0-}) / (1 \text{ ATA}) \end{aligned} \quad [24]$$

Combining equations [23] and [24],

$$n_L^{0-} = \frac{V_L \Gamma_{1 \text{ ATA}}}{R T^\infty z_{1 \text{ ATA}}} (\phi^{0-} - P_1^{0-} - P_{\text{oth}}^{0-}) \quad [25]$$

If we assume that Henry's Law is valid also at the final system pressure  $\phi_x^*$ , then we can write an expression for the Ostwald coefficient at pressure  $\phi_x^*$  that is analogous to equation [25]:

$$n_L^* = \frac{V_L \Gamma_{1 \text{ ATA}}}{R T^* z_{1 \text{ ATA}}} (\phi^* - P_1^* - P_{\text{oth}}^*) \quad [26]$$

Now, we can derive the expression for the Ostwald coefficient in terms of the measured parameters and variables in our experiment. The procedure is identical to that used in section II except that  $n_L^{0-}$  and  $n_L^*$  are represented in the mass balances in terms of  $\Gamma$ , as shown above. The algebra will not be shown this time.

If Henry's Law is considered to apply at all times (ideal behavior), then we can use equation [26] and [25] and solve for  $\Gamma_{1 \text{ ATA}}$ :

$$\Gamma_{1 \text{ ATA}} = \frac{V_G \alpha_3}{V_L \alpha_4} z_{1 \text{ ATA}} \quad [27]$$

where  $\alpha_3$  and  $\alpha_4$  are defined as they were in equation [22]. The Ostwald coefficient at any pressure other than 1 ATA is calculated using the simple proportionality between  $\Gamma$  and pressure that applies in the Henry's Law region.

If there is non-ideal solution behavior at pressure  $\phi_x^*$  then we must use equation [23b] rather than equation [26] to represent  $n_L^*$ , although we still assume the validity of Henry's Law at pressure  $\phi^{0-}$ . Once this is done, we find the following result for the Ostwald coefficient at  $\phi_x^*$ :

$$\Gamma^* = \frac{V_L f_x \Gamma_{1 \text{ ATA}} (\phi^{0-} - P_1^{0-} - P_{\text{oth}}^{0-}) + V_G z_{1 \text{ ATA}} \alpha_3}{(1 \text{ ATA}) V_L} \quad [28]$$

#### IV. Uncertainty in the computed gas solubility: Propagation of error

The partial derivative of H with respect to each parameter has been calculated so that one can determine the sensitivity of the calculated value of H toward the measurement error in each parameter. We assume in the following discussion that H is independent of pressure, and so the derivatives are evaluated from equation [22].

Although the following discussion is concerned with errors in the calculated values of the Henry coefficient H, it is easy to show that the relative errors in the calculated values of the Ostwald coefficient  $\Gamma$  are of equal magnitude, but have the opposite sign. In other words,

$$1/\Gamma (\partial \Gamma / \partial B) = -1/H (\partial H / \partial B)$$

where B is a parameter subject to measurement error.

$$\partial H / \partial V_L = H/V_L \quad [29]$$

$$\partial H / \partial V_G = -H/V_G \quad [30]$$

$$\partial H / \partial T^\infty = H/T^\infty \quad [31]$$

$$\partial H / \partial \phi^{0-} = \frac{-\alpha_1}{\alpha_2 \alpha_3} f_X \quad [32]$$

$$\partial H / \partial \phi_R^\infty = \frac{\alpha_1}{\alpha_2 \alpha_3^2} \left[ \alpha_3 + \left( 1/z_X^\infty - \frac{f_X}{f_R z_R^\infty} \right) \alpha_4 \right] \quad [33]$$

$$\partial H / \partial P_1^{0-} = \frac{\alpha_1}{\alpha_2 \alpha_3^2} f_X \left( \alpha_3 + \alpha_4/z_X^{0+} \right) \quad [34]$$

$$\partial H / \partial P_1^\infty = \frac{-\alpha_1}{\alpha_2 \alpha_3^2} \left( \alpha_3 + \alpha_4/z_X^\infty \right) \quad [35]$$

$$\partial H / \partial \Delta P^\infty = \frac{-\alpha_1}{\alpha_2 \alpha_3^2} \left( \alpha_3 + \alpha_4/z_X^\infty \right) \quad [36]$$



$$\frac{\partial H}{\partial f_R} = \frac{\alpha_2 \alpha_3^2}{\alpha_2 \alpha_3^2 f_R^2 z_R^-} \alpha_4 \varphi_R^- \quad [37]$$

$$\begin{aligned} \frac{\partial H}{\partial f_X} = & \frac{-\alpha_1}{\alpha_2 \alpha_3^2} \left\{ \alpha_3(\vartheta^{0-} - P_1^{0-}) \right. \\ & \left. + [ \varphi_R^- / (f_R z_R^-) - (P_1^{0-} + P_{oth}^{0-}) / z^{0+} + P_{oth}^{0-} / z_X^- ] \right\} \quad [38] \end{aligned}$$

Note that our error analysis is designed only to estimate the error in the calculated H resulting from errors in measuring the individual parameters. A truly comprehensive error analysis would have to address the interactions between parameters. For example, our representation of  $\partial H / \partial T^*$  is actually quite simplistic. The parameter  $T^*$  appears in equation [22] only as a determinant of gas pressure according to an equation of state, and therefore the above expression for  $\partial H / \partial T^*$  accounts only for the errors in computing amounts of gas that result from an error in  $T^*$ . In reality, an error in  $T^*$  means that the water bath temperature is different from its set point, meaning in turn that the Henry's coefficient and the vapor pressure of water are different from their values at the set point temperature. The total error in H resulting from an error in  $T^*$  is seen to be a relatively complicated matter to analyze, and we have not attempted to quantify it. This error is minimized by controlling the experimental conditions as closely as possible: the water bath temperature is maintained to within  $\pm 0.05^\circ\text{C}$  of its set point during the experimental period.

Also note that equation [37] and [38] allow us to calculate errors in H due to the measurement error of a leak on either side of the apparatus. As will be shown later, actual errors in H may be more sensitive toward the "net leakage" represented by  $(f_X - f_R)$  instead.

Let us assign plausible values to the parameters and get numerical values for the derivatives listed as equations [29]-[38]. We want to see whether the experimental results should be more precise at higher or lower total pressure.

Given:  $H = 7.6 \cdot 10^7$  mmHg/mol fraction (approximately the average reported value for nitrogen in water at 37°C)

$$V_L = 120 \text{ cm}^3$$

$$V_G = 30 \text{ cm}^3$$

$$T = 310.15^\circ\text{K} (37^\circ\text{C})$$

$$P^{0-} = 760 \text{ mmHg}$$

$$P_1^{0-} = P_1 = P_1^{\text{vap}} = 47 \text{ mmHg (the vapor pressure of water at } 37^\circ\text{C)}$$

$$P_{\text{oth}}^{0-} = P_{\text{oth}} = 159.6 \text{ mmHg (21\% of } P^{0-})$$

$$f_R = f_X = 1.0 \text{ (i.e., no leaks)}$$

The results are expressed as per cent change in the calculated H per unit of error in the parameter value:

	$P_R$ (mmHg)			
	1000	4000	7600	
$\Delta P$	12.8	173	366	mmHg
$\partial H / \partial V_L$	0.833	0.833	0.833	%/cm <sup>3</sup>
$\partial H / \partial V_G$	-3.33	-3.33	-3.33	%/cm <sup>3</sup>
$\partial H / \partial T$	0.322	0.322	0.322	%/°C
$\partial H / \partial P^{0-}$	-0.440	-0.0326	0.0154	%/mmHg
$\partial H / \partial P_R$	0.440	0.0326	0.0154	%/mmHg
$\partial H / \partial P_1^{0-}$	8.23	0.610	0.289	%/mmHg
$\partial H / \partial P_1$	-8.23	-0.610	-0.289	%/mmHg
$\partial H / \partial \Delta P$	-8.23	-0.610	-0.289	%/mmHg
$\partial H / \partial f_R$	77.9	23.1	20.8	%/%
$\partial H / \partial f_X$	-77.4	-23.0	-20.8	%/%

Clearly, we can expect higher precision at higher pressures.

A question of practical importance is, how much water or tissue should be loaded into the "X" vessel so that experimental precision is maximized? We therefore calculate the partial derivatives for various amounts of water,

assuming a vessel volume of 150 cm<sup>3</sup> (note that H is calculated from the ratio of V<sub>L</sub> to V<sub>G</sub>, not from the individual values of V<sub>L</sub> and V<sub>G</sub>).

Given: H = 7.6 · 10<sup>7</sup> mmHg/mol fraction

T<sup>\*</sup> = 310.15°K (37°C)

ρ<sup>0-</sup> = 760 mmHg

ρ<sub>R</sub><sup>\*</sup> = 1900 mmHg

P<sub>1</sub><sup>0-</sup> = P<sub>1</sub><sup>\*</sup> = P<sub>1</sub><sup>vap</sup> = 47 mmHg (the vapor pressure of water at 37°C)

P<sub>oth</sub><sup>0-</sup> = P<sub>oth</sub><sup>\*</sup> = 159.6 mmHg (21% of ρ<sup>0-</sup>)

f<sub>R</sub> = f<sub>X</sub> = 1.0 (i.e., no leaks)

We calculate the following:

	V <sub>L</sub> = 75 cm <sup>3</sup> V <sub>G</sub> = 75 cm <sup>3</sup>	V <sub>L</sub> = 120 cm <sup>3</sup> V <sub>G</sub> = 30 cm <sup>3</sup>	V <sub>L</sub> = 135 cm <sup>3</sup> V <sub>G</sub> = 15 cm <sup>3</sup>	
ΔP <sup>*</sup>	15.9	61.0	129	mmHg
∂H/∂V <sub>L</sub>	1.33	0.833	0.741	%/cm <sup>3</sup>
∂H/∂V <sub>G</sub>	-1.33	-3.33	-6.67	%/cm <sup>3</sup>
∂H/∂T <sup>*</sup>	0.322	0.322	0.322	%/°C
∂H/∂ρ <sup>0-</sup>	-0.0890	-0.0927	-0.0989	%/mmHg
∂H/∂ρ <sub>R</sub> <sup>*</sup>	0.0890	0.0927	0.0989	%/mmHg
∂H/∂P <sub>1</sub> <sup>0-</sup>	6.39	1.73	0.876	%/mmHg
∂H/∂P <sub>1</sub> <sup>*</sup>	-6.39	-1.73	-0.876	%/mmHg
∂H/∂ΔP <sup>*</sup>	-6.39	-1.73	-0.876	%/mmHg
∂H/∂f <sub>R</sub>	120.0	31.2	14.8	%/%
∂H/∂f <sub>X</sub>	-117.0	-31.0	-15.1	%/%

It appears that errors from most sources can be reduced simply by using a higher liquid-to-gas ratio. (The notable exception is the error in H arising from an error in V<sub>G</sub>; V<sub>G</sub> is calculated by subtracting V<sub>L</sub> from the total volume of vessel X.) The error in H arising from a given absolute error in ΔP<sup>\*</sup> decreases at higher liquid/gas ratios because ΔP<sup>\*</sup> is roughly proportional to V<sub>L</sub>/V<sub>G</sub>, so that the relative error in ΔP<sup>\*</sup> decreases with increasing V<sub>L</sub>/V<sub>G</sub>.

Similarly,  $\partial H/\partial P_1^{0-}$  and  $\partial H/\partial P_1^{*-}$  decrease with increasing liquid/gas ratio because the effect of erroneous values of  $P_1^{0-}$  and  $P_1^{*-}$  is to confound the measurement of  $\Delta P^{**}$ .

The liquid volume probably should not be set above 120 cm<sup>3</sup> in the current vessel, because the use of a greater volume would place some of the liquid in the neck of the vessel (see Figure 1). Since the liquid mass is agitated only by a stirring bar in the bottom of the vessel, the portion within the neck could be poorly mixed, so that passive diffusion might be the primary mechanism of solute transport through that portion. This would necessitate a longer equilibration time, which does not seem desirable since accumulated gas leakage probably is roughly proportional to the duration of the experiment (i.e.,  $f_R$  and  $f_X$  increase with time).

The numerical values of the partial derivatives can be converted to errors in  $H$  based on the manufacturers' claimed precision of the instruments we use. (Of course, the actual precision in our experiment could be substantially better than guaranteed by the manufacturers since we rely on local calibrations over relatively narrow ranges of the measured variables, whereas the specifications normally apply to the full scale. Our precision likewise could fail to meet claimed specifications because of poor quality control or damage to the instruments.) The manufacturers' specifications for our instruments are given in Appendix A. The overall estimated error is the sum of the individual error estimates. We show this calculation for one experimental case:

Given:  $H = 7.6 \cdot 10^7$  mmHg/mol fraction

$$T^* = 310.15^\circ\text{K} (37^\circ\text{C})$$

$$\rho^{0-} = 760 \text{ mmHg}$$

$$\rho_R^* = 1900 \text{ mmHg}$$

$$P_1^{0-} = P_1^* = P_1^{\text{vap}} = 47 \text{ mmHg (the vapor pressure of water at } 37^\circ\text{C)}$$

$$P_{\text{oth}}^{0-} = P_{\text{oth}}^* = 159.6 \text{ mmHg (21\% of } \rho^{0-})$$

$$f_R = f_X = 1.0 \text{ (i.e., no leaks)}$$

$$V_L = 120 \text{ cm}^3$$

$$V_G = 30 \text{ cm}^3$$

We find that  $\Delta P^* = 61.0$  mmHg.

error source

$$V_L (0.833 \text{ \%/cm}^3) \times (\pm 0.1 \text{ cm}^3) = \pm 0.083 \%$$

$$V_G (-3.33 \text{ \%/cm}^3) \times (\pm 0.1 \text{ cm}^3) = \pm 0.333 \%$$

$$T^* (0.322 \text{ \% /}^\circ\text{C}) \times (\pm 0.1^\circ\text{C}) = \pm 0.032 \%$$

$$\rho^{0-} (-0.0927 \text{ \%/mmHg}) \times (\pm 1 \text{ mmHg}) = \pm 0.093 \%$$

$$\rho_R^* (0.0927 \text{ \%/mmHg}) \times (\pm 9 \text{ mmHg}) = \pm 0.834 \%$$

$$P_1^{0-} (1.73 \text{ \%/mmHg}) \times (+ 0.2 \text{ mmHg}) = + 0.346 \%$$

$$P_1^* (-1.73 \text{ \%/mmHg}) \times (+ 0.2 \text{ mmHg}) = - 0.346 \%$$

$$\Delta P^* (-1.73 \text{ \%/mmHg}) \times (\pm 0.031 \text{ mmHg}) = \pm 0.054 \%$$

$$f_R (31.2 \text{ \%/\%}) \times (+ 0.1 \text{ \%}) = + 3.116 \%$$

$$f_X (-31.0 \text{ \%/\%}) \times (+ 0.1 \text{ \%}) = - 3.105 \%$$

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$$\text{total } + 4.89 \%, - 4.88 \%$$

The first total error listed above was obtained by adding together all of the possible positive contributions, and the second total is the sum of all the possible negative contributions. One point to note is that leakage and errors in the assumed partial pressures of water vapor are biased errors. This is because 1) gas leaks out of the system but not in, and 2) the gas phase in vessel X can be below the dew point but not above it. The remaining errors presumably are unbiased.

The major observation from the above examples is that leakage seems to have the greatest potential as an error source. Based on preliminary

measurements of leakage rates, the leakage during an experiment is taken to be 0.1% in the above example, resulting in an error in  $H$  of 3% if only one vessel leaks. Errors of 10% or more would result from a leakage of only 0.5% of the contents of one vessel or the other, which is a very plausible occurrence if an O-ring or valve does not seat perfectly. Note, however, that equal leakage from both vessels produces a net error of close to zero. Obviously, the difference in leakage between the two vessels is far more important than the total leakage from both vessels.

The overall error estimated above applies to a single measurement. Our actual estimate of precision will be obtained through statistical analysis of our entire body of data for each gas. If Henry's Law is valid for a gas over the entire pressure range investigated, then  $H$  equals the slope of a plot of  $y_2^0$  versus  $x_2$ . In that case, we will use linear regression to calculate the slope and use the  $t$  distribution to estimate a confidence interval on the slope. If the  $F$  test indicates statistical support for modelling the system as non-ideal, then we will use a non-linear least-squares minimization technique to fit the data with the expression given at the end of part I of this section. The confidence interval we obtain statistically will almost certainly be more narrow than the uncertainty interval computed above, barring grossly optimistic specifications by the manufacturers.

## V. Measurements of gas leakage

The numerical examples of the previous section demonstrate that the experimental error attributable to leakage is determined by the "net leakage" between flasks R and X. "Net leakage" is defined as  $(f_R - f_X)$ ;  $f_R$  and  $f_X$  are expressed as fractions and are defined by equations [14] and [18]. An examination of those numerical results shows that, to a close approximation,

$$\partial H / \partial f_R + \partial H / \partial f_X = H (f_X - f_R) \phi_R^* / \Delta P^* \quad [39]$$

This can be proven formally under the following assumptions (although the proof will not be shown here):

$$f_X = f_R = 1.0 ; \quad z_R^* = z_X^* = z^{0+} = 1.0 ; \quad P_1^{0-} = P_1^* ; \quad P_{oth}^{0-} = P_{oth}^* .$$

We can make the reasonable assumption that the measurement error  $\Delta f$  is the same for both  $f_R$  and  $f_X$ , i.e.

$$\Delta f = \Delta f_R = \Delta f_X \quad [40]$$

Equation [39] can be rewritten using equation [40] to yield a good estimate of the relative error in the measured value of  $H$  as a function of the leakages from both vessels:

$$\Delta H / H = \Delta f (f_X - f_R) \phi_R^* / \Delta P^* \quad [41]$$

Accordingly, we measure  $(f_X - f_R)$  by pressurizing both vessels simultaneously to the same pressure (without a condensed phase in the X flask), closing the tubing between them (by closing valve V3 in Figure 1), allowing some time for leakage to occur, and then measuring a) the pressure difference between the vessels (using the differential transducer T1 in Figure 1) and b) the pressure in each vessel (using transducers T2 and T3). To evaluate the data, we note



that if  $f_R$  and  $f_X$  are close to 1.0 then the following are true to a close approximation:

$$(f_X - f_R) = - \Delta P^{final} / \rho^{0+} \quad [42]$$

$$f_R = \rho_R^{final} / \rho^{0+} \quad [43]$$

$$f_X = \rho_X^{final} / \rho^{0+} \quad [44]$$

where  $\rho_R^{final}$  = pressure in the R flask at the end of the experiment (mmHg);

$\rho_X^{final}$  = pressure in the X flask at the end of the experiment (mmHg);

$\rho^{0+}$  = initial system pressure (mmHg);

$\Delta P^{final}$  = pressure difference at the end of the experiment,  
 $(\rho_R^{final} - \rho_X^{final})$  (mmHg).

Gas solubility measurements can begin when gas leakage is deemed acceptably small based on the relative error in H. An example calculation is presented:

Given:  $H = 7.6 \cdot 10^7$  mmHg/mol fraction

$T = 310.15^\circ K$  ( $37^\circ C$ )

$\rho^{0-} = 760$  mmHg

$\rho_R = 1900$  mmHg

$P_1^{0-} = P_1 = P_1^{vap} = 47$  mmHg (the vapor pressure of water at  $37^\circ C$ )

$P_{oth}^{0-} = P_{oth} = 159.6$  mmHg (21% of  $\rho^{0-}$ )

$f_R = f_X = 1.0$  (i.e., no leaks)

$V_L = 120$  cm<sup>3</sup>

$V_G = 30$  cm<sup>3</sup>

We find that  $\Delta P = 61.0$  mmHg

$\partial H / \partial f_X = 31.2$  %/%

$\partial H / \partial f_R = 31.8$  %/%

$\partial H / \partial f_R + \partial H / \partial f_X = 31.1 H (f_X - f_R)$  %/%

It already has been computed (near the end of part IV) that the other error sources may contribute up to 2.12% to the relative error in H for this example. If we want no more than 10% total relative error in H, then we will not accept any leak rate that itself produces more than 7.88% error in the

measured H. Accordingly, if it were known somehow that only one of the vessels could leak, then the maximum acceptable leak from the X vessel would be 4.8 mmHg (or  $f_X = 0.9974$ ), and the maximum acceptable leak on the R vessel would be 4.7 mmHg ( $f_R = 0.9975$ ). Based on preliminary leakage measurements, we can take the typical value of  $\Delta f$  (i.e., the error in the assumed value of  $f$ ) to be 0.001 = 0.1%; that is, when computing H we normally would assume zero leakage, or  $f = 1.0$ , and actual values of  $f$  are typically 0.999. Then, the maximum acceptable value of the net leak parameter ( $f_X - f_R$ ) for this example is found to be 0.00253 = 0.253%, or the maximum acceptable differential leak rate between the two vessels is 4.8 mmHg/experimental period.

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## Appendix A: Listing of components in the experimental apparatus

The following types of equipment will be used in measuring gas solubility:

- Electronic pressure transducers
- Two glassware flask assemblies
- Thermometer with 400-series cables
- Two water Baths
- Primary pressure standard (dead weight tester)

The specific components obtained for this project are as follows:

### 1. Electronic pressure transducers

#### A. Differential transducer - MKS, Valley, MD

##### a. Sensor head:

- Series 170, Type 310
- Pressure range: 1000 Torr
- Accuracy:  $\pm 0.05$  % of readings
- Dimensions: 2 1/2" x 3" x 1 3/4"
- Modified in-house for underwater use

##### b. Electronic unit - MKS, Valley, MD

- Type 170M-6C
- Operation Temperature: 15-40°C
- Input: 105-130 VAC
- Output: 0-10 VDC
- Dimensions: 19" x 4 1/2" x 7 1/4"

#### B. Absolute Pressure Gauges - Validyne Engineering Corp., Northridge, CA

- Type: DP15, diaphragm replacement
- Line pressure: 3000 psig
- Pressure Range: variable, depends on which diaphragm is used
- Accuracy: 0.5 % of full scale

### 2. Flask assemblies - NMRI Biomedical Engineering Division, Bethesda, MD

- Pyrex flask, 100 cm<sup>3</sup>
- Stainless steel top

### 3. Thermometer - Yellow Springs Instruments Co., Yellow Spring, OH

- Model 49TA
- Series 400
- Temperature range: 20-43°C
- Accuracy:  $\pm 0.05^\circ\text{C}$  of readings from 30-40°C  
with ambient temperature at 15-35°C
- Dimensions: 3/4" x 9 1/4" x 5 3/4"

### 4. Water baths

#### A. Accumulated bath - NMRI Biomedical Engineering Division, Bethesda, MD

- Plexiglas
- Dimensions: 17" x 13 1/2" x 10 1/2"

B. Supply bath - Forma Scientific Inc., Marietta, OH

- Model 2095
- Temperature range: -20 to +70°C
- Pump capacity: 8 GPM
- Sensitivity : (±) 0.02°C
- Dimensions: 26 5/8" x 20 3/4" X 14 1/2"

5. Primary pressure standard - CEC Instrument Inc., Pasadena, CA

- Type 6-201-0001
- Cylinder piston type 6-001-0002
- Weight set 6-002-0002 (1.5-50 psi)
- Pressure range: 0.3-500 psi
- Accuracy: 0.015% of readings
- Dimensions: 2 1/2 x 3 x 1 3/4"

## Appendix B: Measurement of the volume of vessel X

The volume of our X flask will be determined by measuring the pressure change when a known volume of gas is injected into the vessel. Figure B1 is a diagram of this experiment. A steel-barrelled syringe of volume  $V_1 = 124.99 \text{ cm}^3$  (measured gravimetrically) is used to inject gas through tubing into the vessel. The volume  $V_X$  to be ascertained includes the volume of the tubing connecting the flask with valves V3 and V5 and transducers T1 and T3. Notice that the flask, the valve, and much of the tubing are below the water surface whereas the syringe and some of the tubing are above the surface, in open air. The length-to-diameter ratio of the tubing is high enough that heat transport is much faster in the radial direction than in the axial direction. This fact allows us to assume with confidence that, at steady state, the portion of the system above water is entirely at the ambient temperature while all of the immersed portion is at the water bath temperature. A mass balance around the system can be written as follows:

$$n_{\text{total}}^{\infty} = n_{\text{total}}^{0-} \quad [\text{B1}]$$

and

$$n_{\text{total}} = n_1 + n_2 + n_3 + n_X \quad [\text{B2}]$$

where  $n$  = number of moles of air;

total = subscript denoting the whole system;

1, 2, 3, and X = subscripts denoting portions of the system,  
consistent with Figure B1;

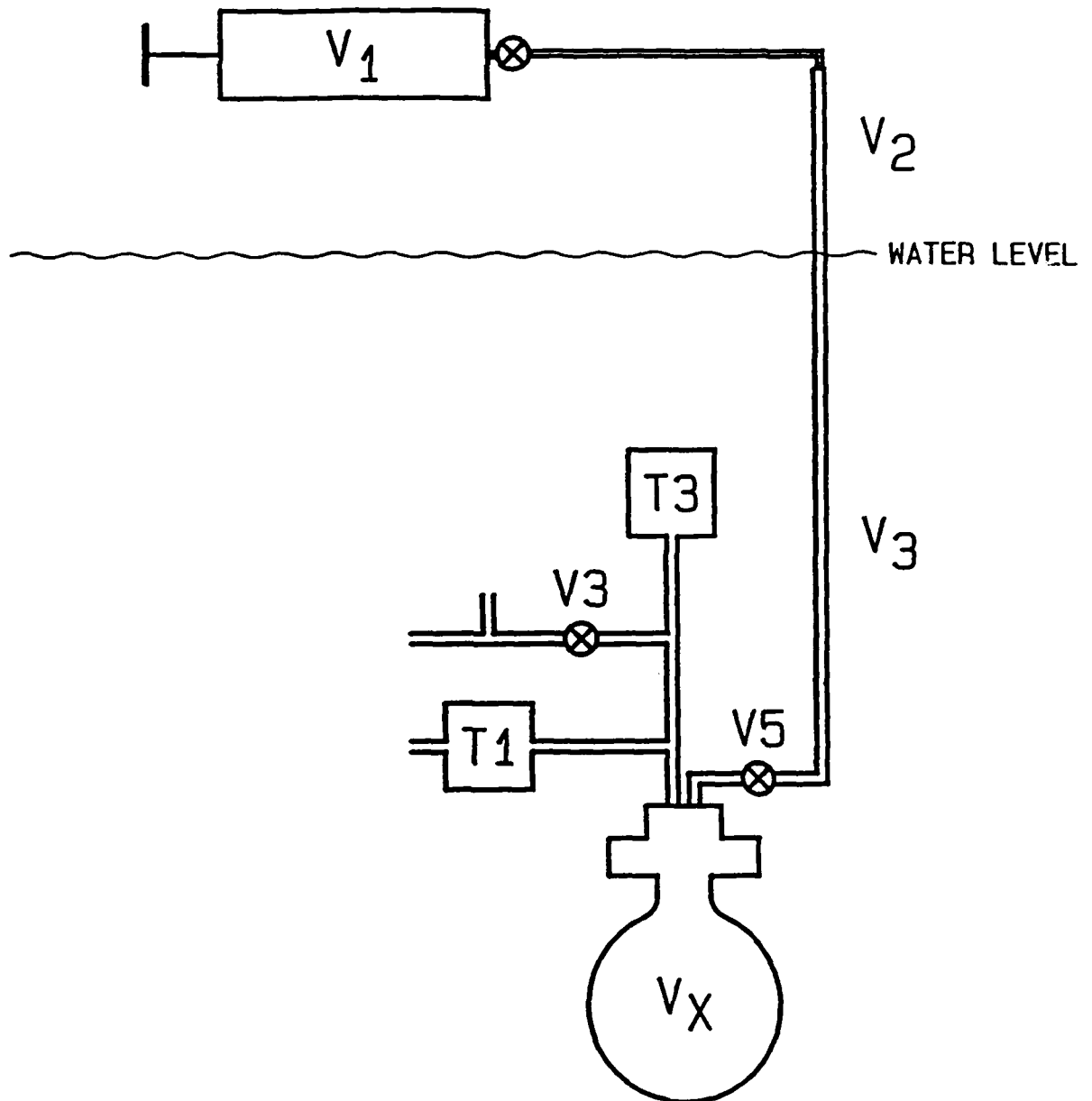
0- = superscript denoting the moment just before injection;

$\infty$  = superscript denoting time infinity.

We also write the following to indicate the difference in system pressure between time = 0- and time =  $\infty$ :

$$p^{\text{final}} = p^{0-} + \Delta p^{\text{final}} \quad [\text{B3}]$$

**FIGURE B1**  
**MEASUREMENT OF THE VOLUME OF VESSEL X**





We measure  $\phi^{\text{final}}$  using both the differential pressure transducer T1 (see Figure 1) and pressure transducer T3, both of which are referenced to the atmosphere during this experiment. Since we see no strong reason to prefer one of these transducers to the other, we pool the data from them.  $\phi^0$  is equal to the ambient pressure  $\phi_{\text{amb}}$  because valve V5 is open to the atmosphere until immediately prior to injecting the air.

We denote the temperature of those portions of the system above water as  $T_{\text{amb}}$  at time = 0- and time =  $\infty$ . The immersed portions have temperature  $T_{\text{bath}}$  at time = 0- and time =  $\infty$ . At intermediate times the temperatures are higher because of the heat evolved upon compression. Finally, we use the ideal gas law to relate pressure and temperature at both time points, and we assume zero leakage from the system. Combining equations [B1]-[B3], we obtain

$$V_X = \frac{\phi_{\text{amb}} T_{\text{bath}}}{\Delta P^{\text{final}}} V_1 - \frac{T_{\text{bath}}}{T_{\text{amb}}} V_2 - V_3$$

where  $\phi_{\text{amb}}$  = ambient pressure (mmHg). The ambient pressure is measured using a mercury manometer and the ambient temperature is measured using a high-precision thermometer certified by the National Bureau of Standards. We measure the volume ( $V_2 + V_3$ ) by filling with water from a graduated syringe after closing the valve shown in Figure B1. We then calculate  $V_2$  from the known diameters of the tubing comprising  $V_2$ , and we obtain  $V_3$  by subtracting  $V_2$  from ( $V_2 + V_3$ ).

Appendix C: Nomenclature for sections II and III of "Data analysis"

- $\rho$  - density ( $\text{g}/\text{cm}^3$ );
- H - Henry's coefficient ( $\text{mmHg}/\text{mol fraction}$ );
- M - molecular weight ( $\text{g}/\text{gmol}$ );
- n - molar quantity of the solute ( $\text{gmol}$ );
- $\phi$  - absolute total pressure ( $\text{mmHg}$ );
- P - absolute partial pressure ( $\text{mmHg}$ );
- $\Delta P$  - differential pressure ( $\text{mmHg}$ );
- R - gas law constant ( $\text{mmHg}\cdot\text{cm}^3/\text{gmol}\cdot^\circ\text{K}$ );
- T - absolute temperature (K)
- V - volume ( $\text{cm}^3$ );
- z - compressibility factor (dimensionless).

subscripts and superscripts:

- G - a subscript that represents the gas phase;
- L - a subscript that represents the liquid phase;
- 1 - a subscript that represents the solvent;
- 2 - a subscript that represents the solute;
- oth - a subscript that represents gases other than the test gas or the solvent vapor;
- R - a subscript that represents the "reference" flask (the one containing only gas);
- X - a subscript that represents the "experimental" flask (the one containing liquid and gas);
- 0- - a superscript that represents the time just before pressurization;
- 0+ - a superscript that represents the time just after pressurization;
- $\infty$  - a superscript that represents infinite time after pressurization in a solubility measurement.